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Categorization (listing) background document : 1, 1, 2-trichloroethane, (CAS: 79-00-5).
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CATEGORIZATION (LISTING) BACKGROUND DOCUMENT

1,1,2-TRICHLOROETHANE

(CAS: 79-00-5)

ONTARIO MINISTRY OF THE ENVIRONMENT

WASTE MANAGEMENT BRANCH

HAZARDOUS WASTE REVIEW UNIT

FEBRUARY 1992

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1.0 SUMMARY OF BASIS FOR CATEGORIZATION

1.1 Listing under Regulation 309

The Ontario Ministry of the Environment (M.O.E.) is considering amending Regulation 309 and listing 1,1,2-trichloroethane in Schedule 1 as a hazardous industrial waste. When 1,1,2-trichloroethane is disposed of as a spent solvent or as still bottoms from the recovery of that same solvent, the waste should be listed under paragraph NA 9302.

1,1,2-trichloroethane is already listed in Schedule 2, Part B of Regulation 309, as a hazardous waste chemical. Hazardous waste chemicals include chemical products or manufacturing intermediates that, from time to time may be off-specification, or otherwise unacceptable for use.

1,1,2-trichloroethane does not exhibit any of the hazardous characteristics (i.e. reactivity, corrosivity, ignitability and leachate toxicity). However, it is a known animal carcinogen. Rats have showed adrenal carcinomas, kidney carcinomas, and varied hemangiosarcomas, while mice have showed an increase in hepatocellular carcinomas and adrenal pheochromocytomas.

If a waste, contaminated with 1,1,2-trichloroethane, is mismanaged either in handling, transportation or disposal, 1,1,2-trichloroethane would enter the environment. The mobility and persistence of 1,1,2-trichloroethane in ground water create a potential hazard.

1.2 Listing under other Canadian legislation

Under the federal Transportation of Dangerous Goods Act (TDGA), 1,1,2-trichloroethane waste is classified as a Class 6.1 waste (i.e. poisonous substance). Waste mixtures containing 100 ppm or more of this substance are classified as Class 9.2 hazardous wastes under the TDGA.

1.3 Listing under U.S. legislation

1,1,2-trichloroethane waste has been listed in the U.S. "Resource Conservation and Recovery Act" (RCRA) as a hazardous waste if disposed of as a spent solvent or as still bottoms from the recovery operation of that solvent. Spent solvent has been defined in the U.S. legislation as follows:

a) the chemical mixture must have a solvent property (i.e. dissolve or mobilize constituents);

b) the chemical mixture must be spent;

c) before use (i.e. at the commercial stage) the chemical mixture must have a total concentration of 10 percent or more of the listed constituents.

2.0 DESCRIPTION OF INDUSTRIAL SECTOR

The sectors responsible for generation of wastes contaminated with 1,1,2-trichloroethane include the industrial sector producing the chemical, the sector using 1,1,2-trichloroethane as an intermediate to manufacture other chemicals, and any other industries using solvents or reagents that are or contain 1,1,2-trichloroethane.

2.1 Production Data

The chemical 1,1,2-trichloroethane is not produced in Canada (PIC, 1987). A total of 24.0 tonnes were imported in 1987 (Statistics Canada, 1987).

The production process used in the U.S. is either by reaction of acetylene gas with a mixture of hydrogen chloride and chlorine in the presence of a catalyst, or by chlorination of ethylene followed by chlorination of 1,2-dichloroethane intermediate. The latter process produces the majority of the 1,1,2-trichloroethane. As a chemical intermediate, 1,1,2-trichloroethane is used in the production of vinylidine chloride. In Canada it is not used as an intermediate (Dow, 1988).

2.2 Solvent Uses

2.2.1 Organic Synthesis

In the organic synthesis process, the solvent acts as a medium in which a reaction takes place, or serves to extract, separate, or purify a material from a mixture. The following processes have been identified in literature (USEPA, 1985) for 1,1,2-trichloroethane:

1) production of cellulose acetate, rubbers and oils;

2) manufacture of polyesters;

3) extraction of vegetable oils;

4) production of fats, waxes, natural resins and alkaloids.

In these processes, the solvent is normally found at trace level, if at all, in the final product.

2.2.2 Miscellaneous process

1,1,2-trichloroethane is also used as a component in the formulation of adhesives for articles used in packaging, transporting and holding food. It is also used as a cleaning and degreasing agent (IARC, 1979).

3.0 WASTE MANAGEMENT PRACTICES

3.1 Waste Generation

The estimate for the waste generation rate is based on the following assumptions made in the U.S. listing document for spent 1,1,2-trichloroethane (USEPA, 1985):

1) the amount of 1,1,2-trichloroethane lost in the liquid waste is estimated at 60% of the total amount of new solvent purchased. This is based on a study that 40% of benzene (a solvent used in applications similar to those of 1,1,2-trichloroethane) purchased by the pharmaceutical industry is lost in media other than liquid waste (i.e. gaseous emissions and residues in the product) (USEPA, 1980b);

2) the concentration of 1,1,2-trichloroethane in the liquid waste stream is estimated at 75%. This is based on ranges for benzene and 2-ethoxyethanol (solvents similar to 1,1,2-trichloroethane) identified in the Industry Studies Data Base (USEPA, 1984);

3) the above evaluation is used for miscellaneous uses as well as for the organic synthesis sector;

4) distillation of spent 1,1,2-trichloroethane generates approximately 70% refined solvent and 30% in still bottoms (NASR, 1982);

5) the amount used in Ontario is proportional to the population i.e. 35% of imports into Canada.

The estimated use of 1,1,2-trichloroethane in Ontario is based on the importation figure (Statistics Canada, 1987) and the relative population of Ontario (i.e. 24 tonnes x 35% = 8.4 tonnes). The amount of 1,1,2-trichloroethane lost in liquid waste is based on the quantity of solvent imported in Ontario and the loss facfor (i.e. 8.4 tonnes x 60% = 5 tonnes). The quantity of waste generated is based on the amount of solvent lost and the concentration of solvent in the waste (i.e. 5 tonnes / 75% = 6.7 tonnes). Since the majority of the spent solvent is recycled by distillation, we estimate that 70% of the spent solvent is recycled as solvent, and 30% of the waste remains as still bottoms (i.e. 6.7 tonnes x 70% = 4.7 tonnes of solvent, and 2 tonnes of still bottoms). The amount

of solvent in the still bottoms represents 0.3 tonne (i.e. 5 tonnes loss - 4.7 tonnes recovered = 0.3 tonne of solvent in still bottoms). A summary of the estimates is illustrated in Figure 1.

3.2 Waste Management

In the organic chemical industries, solvent recovery is widely practised. Other methods of disposal include burning in boilers, incineration and contract hauling (USEPA, 1985).

In reviewing the Generator Registration Reports (GRR, 1988), one generator has registered a 1,1,2-trichloroethane waste produced in the testing of the pore size of one particular grade of paper. The waste is disposed of by an off-site contractor.

4.0 HAZARDOUS PROPERTIES OF THE WASTE

4.1 Hazardous Properties

In a spent solvent, 1,1,2-trichloroethane is typically present at concentrations ranging from 50% to 90%. In the still bottoms from recovery operation, this solvent is present at concentrations ranging from 1 to 20 percent (USEPA, 1985). Taking the worst-case concentration of 50 to 90%, the waste toxicity can be evaluated in terms of toxicity found for pure 1,1,2-trichloroethane.

4.2 Hazardous Characteristics

Under Regulation 309 standards, 1,1,2-trichloroethane does not exhibit any of the four hazardous characteristics, i.e. ignitability, corrosivity, reactivity, or leachate toxicity.

4.3 Physical and Chemical Properties

Selected physical properties and chemical properties are listed in Table 1.

4.4 Environmental Behaviour

4.4.1 Environmental Mobility

Environmental mobility refers to the multimedia partitioning in this paragraph. Using the Fugacity Model (Level 1) (Mackay *et al.*, 1982) it is estimated that 27.2% of 1,1,2-trichloroethane would be in the water medium and 72.4% in air. Since the expected dispersion is in two media, the concern level is high.

4.4.2 Environmental Persistence

1,1,2-trichloroethane undergoes pH-dependent reactions at the environmental pH range. At near neutral conditions (pH less than 5.4), hydrolysis takes place to give an alcohol. Above 5.4, elimination of HCl gives 1,1-dichloroethene (Mabey et al., 1983; Vogel et al., 1987). Of these reactions, the base-catalysed rate is 5.9×10^{-3} L/mole-sec at 25°C and is dominant over hydrolysis above 5.4. The rate of hydrolysis is only 9×10^{-8} L/mole-sec at 80°C (Mabey et al., 1983). The half-life would be 37 years at pH 7 and 135 days at pH 9 in water. This is consistent with the observations that no significant decrease in concentration occurred in 8 days in sterilized water and that no significant degradation was obtained in seawater, (pH 7.4 - 7.7) in 14 days at a temperature of 11 - 12°C (Jensen and Rosenberg, 1975).

1,1,2-trichloroethane showed no biodegradation in both a 24-day modified shake flask test and a river die-away test (Mudder and Musterman, 1982). In two other biodegradation screening tests, one investigator reported no degradation after a long acclimation period (Kawasaki, 1980; Tabak, 1980).

Drilling et al. (1976) studied the degradation of 1,1,2-trichloroethane under simulated atmospheric conditions and they estimated a half-life of 41 hours under conditions of bright sunlight.

Being volatile, the portion of the solvent in the water-air interface zone would escape quite readily to the atmosphere where it would degrade relatively quickly. Consequently, 1,1,2-trichloroethane is expected to persist in ground water only. It would move freely in the environment, and would be particularly difficult to control in groundwater where it would persist indefinitely.

4.4.3 Bioaccumulation

The bioconcentration factors for 1,1,2-trichloroethane, reported in the literature, are less than 10 (Kawasaki, 1980) and 17 (Isnard and Lambert, 1988). Based on a log octanol/water ratio of 2.15, a calculated bioconcentration factor of 25.4 is obtained using the relationship developed by Veith (1980). It is expected that bioaccumulation in aquatic organisms would not be significant.

4.4.4 Environmental Exposure

Most of the waste containing 1,1,2-trichloroethane is landfilled or incinerated. Mismanagement and improper disposal could result in adverse health and environmental effects.

In the event of mismanagement at a landfill site, exposure through volatilization of the solvent can create an air pollution problem, although 1,1,2-trichloroethane is readily destroyed by sunlight (half-life of 41 hours according to Drilling et al. (1976)). In addition, exposure through contamination of ground water is possible. Based on the results of the level 1 fugacity model, the solvent can be found appreciably in two media (72.4% in air and 27.2% in water). Contamination of these two media is a good possibility.

Since 1,1,2-trichloroethane has a relatively high water solubility of 4.5 g/l and the log octanol/water partition coefficient is 2.15, this suggests that 1,1,2-trichloroethane is mobile in aquatic medium (Briggs, 1973). With a resistance to hydrolysis and a relatively low level of biological activity in groundwater, it is expected that 1,1,2-trichloroethane is moderately persistent (U.S. Federal Register, 1985).

In addition 1,1,2-trichloroethane tends to degrade conventional landfill liners and thus the solvent as well as other hazardous substances may leach from land disposal facilities into groundwater.

Since 1,1,2-trichloroethane is mobile in water and moderately persistent, it is expected that it can reach the environmental receptors in harmful concentration (U.S. Federal Register, 1986).

4.5 Toxicity

4.5.1 Acute Lethality

The LC_{50} for 1,1,2-trichloroethane administered by a single oral dose to male and female mice are 378 and 491 mg/kg respectively (White et al, 1985).

The acute 96-hour LC_{50} value for the bluegill sunfish is 40.2 mg/l while the 48-hour LC_{50} value for Daphnia magna is 18.0 mg/l (USEPA, 1980).

4.5.2 Sublethal effects, Plants

Marine and freshwater algae were tested for toxic effects on growth in 96-hour assays. EC_{50} values for marine algae *Chlamydomonas sp., Phaeodactylum tricornutum, Dunaliella sp* and *chlorella ovalis* are 260, 60, 200 and 200 mg/l respectively. The freshwater alga *Chlorella pyrenoidosa* yielded an EC_{50} of 170 mg/l (Adema, 1981).

4.5.3 Sublethal effects, Mammals

Chronic oral exposure in mice affects mainly the liver. Male mice had changes in serum parameters, indicating liver damage and

decreases in immune response parameters. Females showed similar effects as well as increased liver weight. No observed adverse effects levels (NOEL) of 4.4 and 3.9 mg/kg/day have been reported for males and females respectively (White et al., 1985).

4.5.4 Sublethal effects, Non-mammals

Embryo larvae tests conducted with the fathead minnow produced a maximum acceptable toxicant concentration (MATC) value of 9.4 mg/l (USEPA, 1979).

4.5.5 Teratogenicity

A study of the developmental effects of 1,1,2-trichloroethane in animals was done by Seidenberg (1986). Pregnant female mice were orally administered 1,1,2-trichloroethane at 350 mg/kg/day on days 8 through 12 of gestation. The percent survival of neonates from day 1 through day 3 was not affected by treatment, and neither was average neonatal weight measured on day 1 and 3.

4.5.6 Mutagenicity

In vitro mutagenicity assays were negative in Salmonella typhimurium and positive in Sacchararomyces cerevisiae. A cell transformation assay performed in the absence of "metabolic activation" in mouse BALB/C-3T3 cells was negative. A test of DNA repair in cultured rat hepatocytes was positive, but another test with mouse hepatocytes was negative (Williams, 1983).

Adduct formation with calf thymus DNA occurred in vitro at a significant rate (DiRenzo, 1982). In vivo DNA adduct formation was also observed in mouse and rat livers (Mazzullo, 1986). DNA synthesis was inhibited by intratesticular injection of 1,1,2-trichloroethane in the mouse (Borzelleca, 1983).

Other studies have shown however that 1,1,2-trichloroethane is not mutagenic (Crebelli and Carere,1988; Mersch-Sundermann et al., 1989; Mersch-Sundermann, 1989).

Although there are negative as well as positive mutagenic assays, it is evident that 1,1,2-trichloroethane can interact experimentally with mammalian DNA both in vitro and in vivo and may, therefore, be potentially genotoxic.

4.5.7 Carcinogenicity

A bioassay of 1,1,2-trichloroethane for possible carcinogenicity was conducted in mice and rats by NCI (1978). Neoplasms were not observed at statistically significant incidences in rats at doses of up to 92 mg/kg/day, following 78 weeks of oral 1,1,2-trichloroethane administration. A significant increase in

hepatocellular carcinomas occured in mice at doses of 195 or 390 mg/kg/day. Adrenal pheochromocytomas were also observed in mice at 390 mg/kg/day.

Carcinogenicity in rats was also studied by Norpoth (1988), who found that subcutaneous injection of 6.24 mg of 1,1,2-trichloroethane, once a week for 2 years, had no effect on the incidence of sarcomas.

IARC, in its evaluation of reported data, concludes that there is limited evidence of carcinogenicity in mice (IARC, 1979). No carcinogenic evaluation was given for humans because of inadequate data.

4.6 Results of Vector Scoring

A vector scoring system for waste categorization and review has been developed to evaluate the toxicity and exposure of waste to human health and the environment. The results of the vector scoring for 1,1,2-trichloroethane are shown in Table 2. Details of the scoring procedure are presented in the guidance manual (MOE, 1989).

The major toxic effects of concern for 1,1,2-trichloroethane are the carcinogenicity and mutagenicity properties of the chemical. An increase in hepatocellular carcinomas and adrenal pheochromocytomas in mice was observed after oral dosing. The environmental parameters of concern are the mobility and high persistence of the chemical in the environment.

The justification for scoring is presented in Appendix B.

5.0 CONCLUSIONS AND RECOMMENDATIONS

The use of 1,1,2-trichloroethane, as an intermediate in a chemical reaction or as a solvent, generates contaminated wastes.

With an estimated 8.4 tonnes of 1,1,2-trichloroethane being used in Ontario for 1987, the amount of spent solvent generated is estimated to be 6.7 tonnes annually. An estimated 70% or 4.7 tonnes were recovered, leaving 2 tonnes of still bottoms containing about 17% 1,1,2-trichloroethane. Thus a total of 0.3 tonne of 1,1,2-trichloroethane could be released to the environment annually if these wastes were mismanaged.

Because of the high concentration of 1,1,2-trichloroethane in the waste and because of its potential mutagenic effects and its carcinogenic properties, a serious potential hazard would exist by the release of the spent solvent into the environment. In addition,

1,1,2-trichloroethane is considered mobile in the environment based on its solubility in water and volatility. The chemical is also considered persistent in water, based on a half life of 37 years at pH 7.

Based on these considerations, it is recommended that 1,1,2-trichloroethane be listed as a spent solvent in Schedule 1 of Regulation 309 (see Appendix C). 1,1,2-trichloroethane is already listed in Schedule 2, as a hazardous waste chemical.

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TABLE 1: PROPERTIES OF 1,1,2-TRICHLOROETHANE

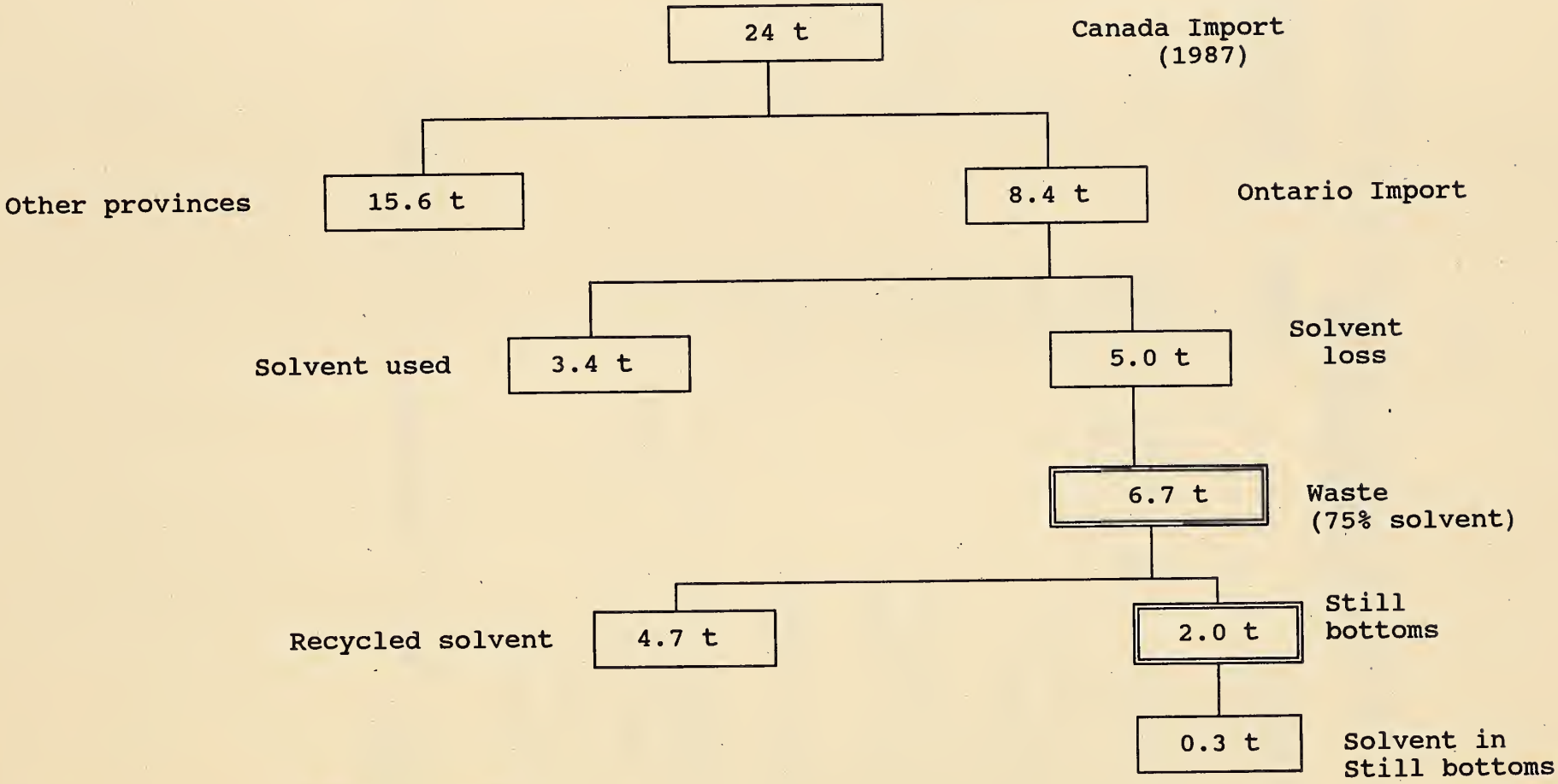
Chemical Abstract #	: 79-00-5
Chemical Abstract Name	: 1,1,2-trichloroethane
Synonyms	: Ethane trichloride, Beta-trichloroethane, 1,2,2-trichloroethane, vinyl trichloride
Trade Names	: Beta-7
Chemical Formula	: $C_2H_3Cl_3$
Molecular Weight	: 133.4
Boiling Point	: 113.5 °C
Melting Point	: -37.0 °C
Density	: 1.44 g/cc
Solubility	: 4.5 g/L in water at 20 °C
Volatility	: vapour pressure 16.73 mm at 20 °C
Log K_{ow}	: 2.17 (Callahan, 1979)

TABLE 2: RESULTS OF VECTOR SCORING OF 1,1,2-TRICHLOROETHANE

Parameter	Score	Concern Levels+
1. Environmental Mobility	10	≥ 7
2. Environmental Persistence	10	≥ 7
3. Bioaccumulation	0	≥ 7
4. Environmental Exposure	7	≥ 7
5. Acute lethality	2	≥ 6
6. Sublethal effects plants	0	≥ 4
7. Sublethal effects mammals	6	≥ 4
8. Sublethal effects non-mammals	0	≥ 4
9. Teratogenicity	0	≥ 2
10. Mutagenicity	6	≥ 6
11. Carcinogenicity	2	≥ 2

(+): concern levels established for the listing of hazardous wastes.

Figure 1: Estimated Waste Generation



Note: t : metric tonne

: 1,1,2 - trichloroethane

: waste containing 1,1,2 - trichloroethane

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Appendix A:

U.S. REGULATIONS

The USEPA has defined spent solvents as those solvents that are used for their "solvent" properties, that is to solubilize (dissolve) or mobilize other constituents (for example, solvents used in degreasing, cleaning, fabric scouring, as diluents, extractants, reaction and synthesis media). A solvent is considered "spent" when it has been used and is no longer fit for use without being regenerated, reclaimed or otherwise reprocessed.

The listing of spent solvents was originally drafted with the intention to include technical grade or pure forms of the solvent. After December 31, 1985, the listed solvents are to include mixtures containing a total of ten percent or more of the listed solvents. The ten percent threshold applies to solvent mixtures, before use. The agency took this position based on data which indicate that solvent mixtures commercially used, typically contain more than ten percent total solvents.

Source:

U.S. Federal Register, Final Rule, Vol. 51, Feb. 25, 1986, p.6537-6542.

Appendix B: Justification for Vector Scoring of 1,1,2-Trichloroethane

Parameter	Score	Justification
1. Environmental Mobility	10	Using Level 1 Fugacity Model, 72.4% in air and 27.4% in water.
2. Environmental Persistence	10	Half life of 37 years at pH 7, in ground water.
3. Bioaccumulation	0	BCF of 17.
4. Environmental Exposure	7	Easy pathway between the contaminants sources and receptors.
5. Acute lethality	2	48-hour LC_{50} for *Daphnia Magna* is 18 mg/l (USEPA, 1980)
6. Sublethal effects plants	0	EC_{50} of 170 mg/l for freshwater alga *Chlorella pyrenoidosa*.
7. Sublethal effects mammals	6	NOEL of 3.9 mg/kg.
8. Sublethal effects non-mammals	0	MATC value for fathead minnows of 9.4 mg/l (AWQC, 1979).
9. Teratogenicity	0	No effects at 350 mg/kg/day.
10. Mutagenicity	6	DNA adduct formation in vitro and in vivo.
11. Carcinogenicity	2	Carcinomas in only one species (mice).

Appendix C: Proposed Amendment to Regulation 309

Schedule 1, Paragraph NA9302

"The following spent halogenated solvents: tetrachloro-ethylene, methylene chloride, trichloro-ethylene, 1,1,1-trichloroethane, **1,1,2-trichloroethane**, chlorobenzene, 1,1,2-trichloro-1,2,2-trifluoroethane, ortho-dichlorobenzene, trichloro-fluoromethane; and the still bottoms from the recovery of these solvents."

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